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(54) Title: HYDRAULIC CEMENT AND COMPOSITION EMPLOYING THE SAME

(57) Abstract

A hydraulic cement is formed from a Class C fly ash and an alkali metal activator. Mortar and concrete compositions can be prepared with this hydraulic cement. The cement is particularly useful in producing mortar and concrete compositions that achieve high strengths in a short time.

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HYDRAULIC CEMENT AND COMPOSITION EMPLOYING THE SAME

BACKGROUND OF THE INVENTION

Hydraulic cements, such as portland cement and blended portland cement and hydraulic cements, consisting of pozzolans, have, for many years, been used as an essential ingredient of the mortar and concrete used for construction of structures, highways, etc. In many instances, fly ash has been used as the pozzolanic component in blended hydraulic cements, and as a mineral admixture to replace part of the more expensive portland cement used in mortar or concrete. The use of fly ash, in place of part of the portland cement or as a constituent in blended cements reduces the large amount of energy required to produce the for mortar and concrete. hydraulic cements required However, the prior art has taught that no more than 35 to 45 per cent of the portland cement can be replaced with fly ash. According to the teachings of the prior art, when more fly ash than that is employed, the resulting mortars and concretes do not have sufficient strength.

It now has been found, however, according to the present invention, that a hydraulic cement where all of the portland cement or blended hydraulic cement is replaced with fly ash can be formed by activating a Class C fly ash with an alkali metal containing material. There is, consequently, a further reduction of cost and energy requirements.

BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, a hydraulic cement composition is provided consisting essentially of Class C fly ash and an alkali metal activator. The activator consists of one or more materials selected from the class consisting of potassium hydroxide, potassium carbonate, sodium hydroxide, sodium carbonate and portland cementkiln dust. The amount of alkaline metal activator employed, per 100 parts of the total composition, can vary from about 1/2 to 10 parts, by weight. In general, when one of the listed materials other than portland cement kiln dust is employed, no more than 4 parts by weight are used, preferably, between 1/2 and 3 parts, by weight.

Included in the formulation are appropriate set control materials such as citric acid, borax, Cormix, WRDA, Daracem 100, or other admixtures commonly used in concrete formulations. The admixture should comprise from about 1/2 to 3 parts, by weight, of at least one of the referenced materials per 100 total parts of cement composition.

This hydraulic cement achieves both high early strengths and high ultimate strengths. It can be utilized for rapid concrete repair or construction. This cement can be utilized in the production of precast and prestressed concrete, with or without heat curing.

The cement composition of the present invention includes the following components, by weight:

From 90 to 97 parts Class C fly ash

From 1/2 to 10 parts alkali metal activator

From 1/2 to 3 parts admixture

In addition to the materials in the above formulation, other materials can be added to the composition, as, for example, retarders and water reducers commonly used in concrete formulations. Various substitutions are also possible for

the required materials. While potassium hydroxide is the preferred alkaline metal activator, sodium hydroxide, sodium carbonate, potassium carbonate, and portland cement kiln stack dust can replace all or part of the potassium hydroxide. As indicated, when any of the referenced materials other than portland cement kiln stack dust is employed, the amount of material is generally from 1/2 to 4 parts, by weight, for each 100 part of the cement composition, preferably from about 1/2 to 3 parts, by weight.

When the hydraulic cement of the present invention is used in concrete or mortar, the resulting hardened material has sufficient strength that it can be put into service a few hours after being placed. This strength can be obtained with or without heat curing.

DESCRIPTION OF PREFERRED EMBODIMENTS

The hydraulic cement of the present invention has, as previously indicated, the following components by weight:

- 90 to 97 parts Class C fly ash
- 1/2 to 10 parts alkali metal activator
- 1/2 to 3 parts admixture

The fly ash is a Class C fly ash as classified in ASTM C-618.

When potassium hydroxide is used as the alkali metal activator, it can be in the form of flakes, pellets, or water solution. Sodium hydroxide, potassium carbonate, sodium carbonate, and high alkali kiln stack dusts, such as those collected during the production of portland cement, can also be utilized as a source of alkali metal ions.

A preferred admixture is citric acid which can be in any available grade, such as fine crystal, powder, or liquid. Salts of citric acid can be used. Borax, a mineral with the composition $Na_20.2B_20_3.10H_20.$, can be used in any available grade and can be replaced, all or in part, by other available admixtures that control the set of concrete mixtures. The major distinction between the cement of the present invention and prior art is the use of fly ash with an alkali metal activator to produce a hydraulic cement with very early strengths, and without portland cement.

All of the components can be interground or interblended and used as a complete cement without additional
admixtures. In an alternative, the sources of the alkali
metal ion, citric acid, and borax, or other admixtures, may
be added at the concrete mixer, in a dry or liquid form, as
an admixture or as a second component. When all of the
materials are blended together, so that only water and
aggregate are required to obtain a mortar or concrete, the
control problems that can occur when materials are mixed in
the field are eliminated or minimized. On the other hand,
when the various materials are blended in the field, there
is an economy of storage and shipping. In addition, the two
component procedure does allow for greater control of
working time.

The following are given as examples of formulations of the hydraulic cement of the present invention. They should be considered only as illustrative and not as limiting, in any way, the full scope of the invention as covered in the appended claims.

All parts are by weight. The Class C fly ash used in the following examples had the properties set forth below:

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CLASS C FLY ASH

CHEMICAL	ANAL	ZSIS	(AS	RECEIV	ED	<u>8)</u>
Si02						60
Al ₂ 0 ₃				:	20.	47
Fe ₂ 0 ₃					5.	44
Ca0				:	21.	54
Mg0					4.	61
so ₃ (by	LECO	Furr	ace	2.12%)	1.	71
Na_20						78
K ₂ 0					Ο.	52
TiO2					1.	05
Sr0				•	Ο.	65
Loss				1	0.	41

FINENESS

SIEVE No. 325 = 82.3% passing BLAINE = $4270 \text{ cm}^2/\text{g}$

X-RAY DIFFRACTION - CRYSTAL STRUCTURES PRESENT:

- 1) SiO₂ (silicon oxide)
- 2) Fe₂0₃ (iron oxide)
- 3) Mg0 (magnesium oxide)
- 4) Ca0 (calcium oxide)
- 5) TiO₂ (titanium oxide)

EXAMPLE 1

A cement mixture was formed consisting of:

- 96.29 parts Class C fly ash
 - 1.41 parts potassium hydroxide
 - 1.28 parts citric acid
 - 1.02 parts borax

A concrete was prepared employing the cement of Example 1 and other necessary materials as indicated below:

825 parts of cement as Example 1

1213 parts sand

1820 parts gravel

142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 25 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths as follows:

Ac	<u>je</u>	Streng	<u>th</u>
3	hours	1,800	psi
4	hours	2,000	psi
1	day	4,000	psi
3	days	6,600	psi
7	days	8,800	psi
28	days	10,400	psi

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured in steam at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths as follows:

A	g <u>e</u>	Streng	<u>jth</u>
3	hours	3,600	psi
4	hours	4,800	psi
1	day	5,700	psi
3	days	6,600	psi
7	days	7,600	psi
28	days	9,400	psi

A cement mixture was formed consisting of:

- 95.98 parts Class C fly ash
 - 1.40 parts potassium hydroxide
 - 1.28 parts citric acid
 - 1.02 parts borax
 - 0.05 part Cormix SP-1P

Cormix 2000 SP-1P is a sodium salt of a copolymer of an unsaturated carboxylic acid and the hydroxyaklyl ester of such an acid. Cormix meets the requirements of ASTM C-494 as a Type G admixture (water-reducing, high range, and retarding admixture).

EXAMPLE 4

A concrete was prepared employing the cement of Example 3 and other necessary materials as indicated below:

- 827 parts of cement of Example 3
- 1362 parts sand
- 1669 parts gravel
 - 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 20 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 2,000 psi at 4 hours, 4,200 psi at 1 day, and 7,600 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperatures (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 5,000 psi at 4 hours, 6,500 psi at 1 day, and 7,600 psi at 7 days.

A cement mixture was formed consisting of:

- 95.98 parts of Class C fly ash
 - 1.40 parts potassium hydroxide
 - 1.28 parts citric acid
 - 1.02 parts borax
 - 0.05 part Cormix 2000 cp

The Cormix 2000 is the sodium salt of a copolymer of an unsaturated carboxylic acid and the hydroxyalkyl ester of that acid. The material meets the requirements of ASTM C-494-86, as a type G admixture, one which is water-reducing, high range, and retarding.

EXAMPLE 6

A concrete was prepared employing the cement of Example 5 and other necessary materials as indicated below:

- 827 parts of cement of Example 5
- 1362 parts sand
- 1669 parts gravel
 - 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 32 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of __1,300 psi at 4 hours, 2,800 psi at 1 day, and 5,5000 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 2,200 psi at 4 hours, 3,200 psi at 1 day, and 4,500 psi at 7 days.

A cement mixture was made consisting of:

- 95.98 parts Class C fly ash
 - 1.40 parts potassium hydroxide
 - 1.28 parts citric acid
 - 1.02 parts borax
 - 0.05 part WRDA-79P

WRDA 79-P is a modified lignosulfonate, with catalyst. meets the requirements of ASTM C-494 as a Type A admixture (water-reducing admixture) and Type D admixture (waterreducing and retarding admixture).

EXAMPLE 8

A concrete was prepared employing the cement of Example 7 and other necessary materials as indicated below:

- 827 parts of cement of Example 7
- 1362 parts sand
- 1669 parts gravel
 - 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 28 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 1,900 psi at 4 hours, 3,600 psi at 1 day, and 7,600 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperatures (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured This concrete had in ambient (73°F) air until tested. compressive strengths of 2,900 psi at 4 hours, 4,200 psi at 1 day, and 5,800 psi at 7 days.

A cement mixture was made consisting of:

- 95.98 parts Class C fly ash
 - 1.40 parts potassium hydroxide
 - 1.28 parts citric acid
 - 1.02 parts borax
- 0.05 part Daracem 100P

Daracem 100P is a dispersion of sulfonated napthalene formaldehyde condensate, a gluconate, and a lignosulfonate. Daracem 100P meets the requirements of ASTM C-494 as a Type G admixture (water-reducing high range, and retarding admixture).

EXAMPLE 10

A concrete was prepared employing the cement of Example 9 and other necessary materials as indicated below:

- 827 parts of cement of Example 9
- 1362 parts sand
- 1669 parts gravel
 - 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 30 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 1,900 psi at 4 hours, 3,800 psi at 1 day, and 7,700 psi at 7 days.

The remaining concrete was cast in molds and stored at 'ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 3,800 psi at 4 hours, 4,900 psi at 1 day, and 6,200 psi at 7 days.

A cement mixture was made consisting of:

- 95.98 parts Class C fly ash
 - 1.40 parts potassium hydroxide
- 1.28 parts citric acid
- 1.02 parts borax
 - 0.025 part Cormix 2000 cp
 - 0.025 part Cormix SP-1P

EXAMPLE 12

A concrete was prepared employing the cement of Example 11 and other necessary materials as indicated below:

- 827 parts of cement of Example 11
- 1362 parts sand
- 1669 parts gravel
 - 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 25 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 2,400 psi at 4 hours and 5,000 psi at 1 day.

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 5,100 psi at 4 hours and 7,300 psi at 1 day.

EXAMPLE 13

A mortar was prepared employing the cement of Example 1 and other necessary materials as indicated below:

- 1480 parts of the cement of Example 1
- 2274 parts sand
 - 246 parts water

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The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

<u>Age</u>		Streng	th
2	hours	2,000	psi
3	hours	2,300	psi
4	hours	2,700	psi
1	day	5,400	psi
3	days	8,400	psi
7	days	10,000	psi
28	days	13,200	psi

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

Age	Strength
4 hours	4,400 psi
1 day	5,800 psi
28 days	12,800 psi

EXAMPLE 14

A cement mixture was made consisting of:

- 96.41 parts Class C fly ash
 - 1.28 parts potassium hydroxide
 - 1.28 parts citric acid
 - 1.03 parts borax

EXAMPLE 15

A mortar was prepared employing the cement of Example 14 and other necessary materials as indicated below:

- 1479 parts of the cement of Example 14
- 2275 parts sand
- 246 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 37 minutes. Part of the mortar was cast in molds and cured at ambient temperatures (73°F). This mortar had compressive strengths as follows:

Age		Streng	<u>jth</u>
2	hours	1,800	psi
3	hours	2,200	psi
4	hours	2,400	psi
1	day	4,700	psi
	days	7,400	psi
	days	8,500	psi
	days	12,000	psi

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

Age		Streng	<u>jth</u>
	hours	3,400	psi
1	day	5,000	psi
28	days	12,000	psi

EXAMPLE 16

A cement mixture was made consisting of:

- 96.53 parts Class C fly ash
- 1.16 parts potassium hydroxide
- 1.28 parts citric acid
- 1.03 parts borax

A mortar was prepared employing the cement of Example 16 and other necessary materials as indicated below:

1477 parts of the cement of Example 16

2276 parts sand

247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 45 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

<u>Age</u>		Streng	<u>ith</u>
2	hours	1,500	psi
3	hours	2,000	psi
4	hours	2,200	psi
1	day	4,200	psi
3	days	6,600	psi
7	days	8,300	psi
28	days	11,700	psi

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

Age		Strength		
4	hours	3,100	psi	
1	day	5,200	psi	
28	days	11,100	psi	

A cement mixture was prepared consisting of:

96.66 parts Class C fly ash

- 1.03 parts potassium hydroxide
- 1.28 parts citric acid
- 1.03 parts borax

EXAMPLE 19

A mortar was prepared employing the cement of Example 18 and other necessary materials as indicated below:

1476 parts of the cement of Example 18

2277 parts sand

247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 60 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

Age		Streng	<u>jth</u>
2	hours	1,300	psi
3	hours	1,800	psi
4	hours	2,200	psi
1	day	4,000	psi
3	days	6,300	psi
	days	8,200	psi
28	days	11,700	psi

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

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Age		Streng	<u>jth</u>
_	hours	2,400	psi
1	day	5,300	psi
28	davs	11,200	psi

EXAMPLE 20

A cement mixture was prepared consisting of:

- 96.79 parts Class C fly ash
 - 0.90 part potassium hydroxide
 - 1.28 parts citric acid
 - 1.03 parts borax

EXAMPLE 21

A mortar was prepared employing the cement of Example 20 and other necessary materials as indicated below:

1475 parts of the cement of Example 20

2278 parts sand

247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 110 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

<u>Age</u>		Streng	Strength	
2	hours	160	psi	
3	hours	1,200	psi	
4	hours	1,600	psi	
1	day	3,600	psi	
3	days	5,400	psi	
7	day	6,900	psi	
28	days	9,700	psi	

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one Specimens were then cured in ambient and one-half hours. (73°F) air until tested. This mortar had compressive strengths as follows:

Age		<u>Strength</u>		
	hours	2,000	psi	
1	day	5,000	psi	
28	days	9,900	psi	

EXAMPLE 22

A cement mixture was prepared consisting of:

- 96.91 parts Class C fly ash
- 0.77 part potassium hydroxide
- 1.28 parts citric acid
- 1.03 parts borax

EXAMPLE 23

A mortar was prepared employing the cement of Example 22 and other necessary materials as indicated below:

- 1474 parts of the cement of Example 22
- 2279 parts sand
 - 247 parts water

The various materials were mixed in a mortar mixer. mortar had an open or working time of 135 minutes. the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

Age	Strength	
2 hours	not set	
3 hours	640 psi	
4 hours	1,400 psi	
1 day	3,100 psi	
3 days	4,900 psi	
7 days	5,500 psi	
28 days	8,900 psi	

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. The mortar had compressive strengths as follows:

<u>Age</u>	<u>Strength</u>		
4 hours	1,000 psi		
1 day	3,100 psi		
28 days	7,900 psi		

EXAMPLE 24

A mortar was prepared as in Example 19 and cast in molds at ambient temperature (73°F). The specimens were cooled at 5°F and maintained at that temperature until shortly before testing. At that time the specimens were warmed to 73°F and tested for compressive strength. The mortar had strengths of 700 psi at 4 hours, 1,200 psi at 1 day, 1,500 psi at 7 days, and 3,400 psi at 28 days.

EXAMPLE 25

A cement mixture was prepared consisting of:

- 96.91 parts Class C fly ash
- 0.77 part sodium hydroxide
- 1.29 parts citric acid
- 1.03 parts borax

EXAMPLE 26

A mortar was prepared employing the cement of Example : 25 and other necessary materials as indicated below:

- 1467 parts of the cement of Example 25
- 2268 parts sand
 - 265 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 40 minutes. The mortar was cast in molds and cured at ambient temperatures (73°F). This mortar had compressive strengths of 1,700 psi at 2 hours, 2,000 psi at 3 hours, 2,200 psi at 4 hours, and 4,100 psi at 1 day.

EXAMPLE 27

A cement mixture was prepared consisting of:

- 94.95 parts Class C fly ash
- 3.79 parts potassium carbonate
- 1.26 parts citric acid

EXAMPLE 28

A mortar was prepared employing the cement of Example 27 and other necessary materials as indicated below:

- 1482 parts cement of Example 27
- 2246 parts sand
 - 272 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. The mortar was mixed, cast in molds and cured at ambient temperature (73°F). The mortar had compressive strengths as follows:

Age	Strength		
2 hours	1,100 psi		
3 hours	1,500 psi		
4 hours	1,700 psi		
1 day	4,100 psi		
3 days	5,800 psi		
7 days	8,400 psi		

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EXAMPLE 29

A cement mixture was prepared consisting of:

90.69 parts Class C fly ash

7.98 parts kiln stack dust

1.33 parts citric acid

The kiln stack dust had the following properties: Specific Gravity = 2.63

CHEMICAL

Leco $S0_3 = 11.70$ %

Atomic Absorption Na₂0 = 2.25%

Atomic Absorption $K_20 = 25.2$ %

Loss = 12.25%

Moisture Content = 0.57%

Water Soluble Alkali: Na₂0 = 2.1%

Water Soluble Alkali: K20 = 20.4%

FINENESS

Sieves: No. 200 = 90.5%

No. 325 = 86.3%

Blaine: $18,619 \text{ cm}^2/\text{g}$

X-RAY DIFFRACTION; CRYSTAL STRUCTURES PRESENT:

- 1) Calcium Carbonate =
- 2) Potassium Sulfate
- 3) Potassium Sodium Sulfate

EXAMPLE 30

A mortar was prepared employing the cement of Example 29 and other necessary materials as indicated below:

1424 parts cement of Example 29

2273 parts sand

303 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. The mortar was mixed, cast in molds and cured at ambient temperature (73°F). The mortar had compressive strengths of 1,300 psi at 2 hours, 1,500 psi at 3 hours, and 1,600 psi at 4 hours.

EXAMPLE 31

A cement mixture was prepared consisting of:

- 92.02 parts Class C fly ash
 - 6.65 parts kiln stack dust
 - 1.33 parts citric acid

EXAMPLE 32

A mortar was prepared employing the cement of Example 31 and other necessary materials as indicated below:

- 1431 parts cement of Example 31
- 2284 parts sand
 - 285 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. mortar was mixed, cast in molds and cured at ambient temperature (73°F). The mortar had compressive strengths of 1,200 psi at 2 hours, 1,500 psi at 3 hours, 1,800 psi at 4 hours, and 4,000 psi at 1 day.

While specific examples of the present invention have been shown and described, they should be considered as merely illustrative, and not as limiting, in any way, the full scope of the invention as set forth in the appended claims.

WHAT IS CLAIMED AS NEW IS:

- 1. A hydraulic cement comprising, by weight:
 From about 90 to 97 parts Class C fly ash
 From about 1/2 to 10 parts alkali metal activator
 From about 1/2 to 3 parts admixture
- 2. The hydraulic cement of Claim 1 wherein the alkali metal activator is portland cement kiln dust.
- 3. The hydraulic cement of Claim 1 wherein the alkali metal activator is from 1/2 to 4 parts of at least one material selected from the group consisting of potassium hydroxide, potassium carbonate, sodium hydroxide, and sodium carbonate.
- 4. The hydraulic cement of Claim 3 wherein the amount is from about 1/2 to 3 parts.
- 5. The hydraulic cement of Claim 3 wherein the alkali metal activator is potassium hydroxide.
- 6. The hydraulic cement of Claim 1 wherein the admixture is selected from the class consisting of citric acid, borax, Cormix, WRDA, and Daracem 100.
- 7. The hydraulic cement of Claim 6 wherein the admixture is from about 1/2 to 1 1/2 parts citric acid and from about 1/2 to 1 1/2 parts borax.

- 8. A two part composition for hydraulic cement, wherein said two parts are blended prior to preparation of the cement, comprising:
 - a. a first part comprising from 90 to 97 parts, by weight, Class C fly ash; and
 - b. a second part comprising:
 - (1) from about 1/2 to 10 parts alkali metal activator; and
 - (2) from about 1/2 to 3 parts admixture.
 - 9. The composition of Claim 8 wherein the alkali metal activator is portland cement kiln dust.
- 10. The composition of Claim 8 wherein the alkali metal activator is from 1/2 to 4 parts of at least one material selected from the group consisting of potassium hydroxide, potassium carbonate, sodium hydroxide, and sodium carbonate.
- 11. The composition of Claim 8 wherein the amount is from about 1/2 to 3 parts.
- 12. The composition of Claim 8 wherein the alkali metal activator is potassium hydroxide.
- 13. The composition of Claim 8 wherein the admixture is selected from the class consisting of citric acid, borax, Cormix, WRDA, and Daracem 100.
- 14. The composition of Claim 8 wherein the admixture is from about 1/2 to 1 1/2 parts citric acid and from about 1/2 to 1 1/2 parts borax.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 88/04055

	FICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶	
According to	FICATION OF SUBJECT MATTER (II Social National Classification and IPC of International Patent Classification (IPC) or to both National Classification and IPC	-
IPC4:	C 04 B 7/26	
	OTA BOUED	
(I. FIELDS	Minimum Documentation Searched	
Classification	n System Classification Symbols	
IPC ⁴	C 04 B	
	Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched	•
III. DOCU	MENTS CONSIDERED TO BE RELEVANT 9	Relevant to Claim No. 13
Category *	MENTS CONSIDERED TO BE RELEVAN. Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	
х	US, A, 4028130 (WEBSTER et al.) 7 June 1977 see claim 20	1,2,8,9
х	Chemical Abstracts, volume 95, no. 8, August 1981, (Columbus, Ohio, US), A. Derdacka-Grzymek et al.: "Cementless binding material from fly ash", see page 295, abstract 66734k, & CemWapno-Gips 1980,	1,3,8,10
A	(8-9), 220-2 US, A, 4432800 (KNELLER et al.) 21 February 1984 see claim 1	1-3,8-10
A	US, A, 4101332 (NICHOLSON) 18 July 1978 see claims 1-3	1,2,8,9
A		1,3,6,8,
"A" do co co co fil	ocument defining the general state of the art which is not considered to be of particular relevance partier document but published on or after the international ling date ocument which may throw doubts on priority claim(s) or other hitch is cited to establish the publication date of another itation or other special reason (as specified) ocument referring to an oral disclosure, use, exhibition or other means ocument published prior to the international filling date but after than the priority date claimed RTIFICATION The Actual Completion of the International Search The February 1989 Signature of Authorizet Office	ional Search Report
Internati	ional Searching Authority	
l	EUROPEAN PATENT OFFICE	DCG VAN DER PUTTEN

Category *	ENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND S Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	see claim 1; page 2, line 105 - page 3, line 27	
A	GB, A, 1505861 (I.U. TECHNOLOGY CORP.) 30 March 1978	
A	US, A, 4268316 (WILLS, Jr) 19 May 1981	
		·
	-	
	• -	-
	٠	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 8804055

SA 25593

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/03/89

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4028130	07-06-77	DE-A- 2456225 FR-A- 2278648 AU-A- 7548174 GB-A- 1455917 CA-A- 1035796	12-06-75 13-02-76 20-05-76 17-11-76 01-08-78
US-A- 4432800	21-02-84	None	
US-A- 4101332	18-07-78	US-A- 4018617 FR-A,B 2339708 DE-A- 2703908 AU-A- 2166477 JP-A- 52115827 CA-A- 1082746 GB-A- 1576234 US-E- 30943	19-04-77 26-08-77 04-08-77 03-08-78 28-09-77 29-07-80 01-10-80 25-05-82
GB-A- 2051031	14-01-81	BE-A- 883533 FR-A,B 2457845 DE-A,C 3020384 NL-A- 8003179 JP-A- 55162456 AU-A- 5880480 US-A- 4306912 SE-A- 8003922 CA-A- 1150327 AU-B- 537598 CH-A- 644573 SE-B- 447097	15-09-80 26-12-80 11-12-80 02-12-80 17-12-80 04-12-80 22-12-81 01-12-80 19-07-83 05-07-84 15-08-84 27-10-86
GB-A- 1505861	30-03-78	None -	
US-A- 4268316	19-05-81	None	